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Title: Airborne Sulfur Trace Species Intercomparison Campaign: Sulfur Dioxide, Dimethylsulfide, Hydrogen Sulfide, Carbon Disulfide, and Carbonyl Sulfide

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Discipline: Atmosphere-Instrumentation Intercomparison

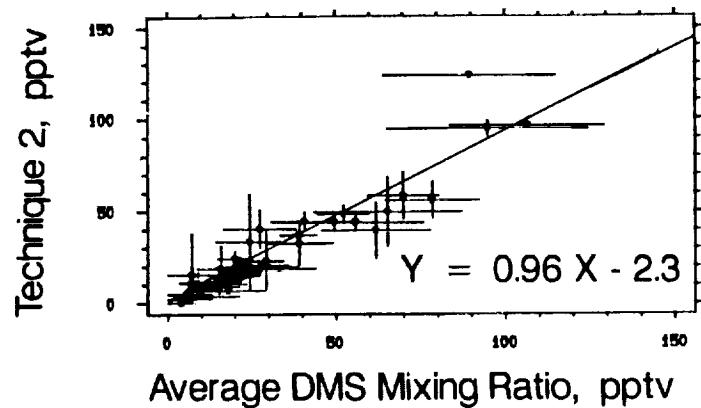
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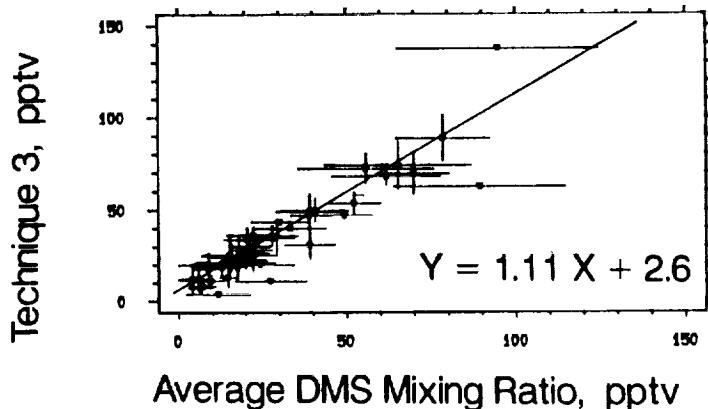
Results from an airborne intercomparison of techniques to measure tropospheric levels of sulfur trace gases are presented. The intercomparison was part of the National Aeronautics and Space Administration (NASA) Global Tropospheric Experiment (GTE) and was conducted during the summer of 1989. The intercomparisons (Chemical Instrumentation Test and Evaluation--CITE-3) were conducted on the Wallops Electra aircraft during flights from Wallops Island, Virginia, and Natal, Brazil. Sulfur measurements intercompared included sulfur dioxide (SO_2), dimethylsulfide (DMS), hydrogen sulfide (H_2S), carbon disulfide (CS_2), and carbonyl sulfide (OCS). Measurement techniques ranged from filter collection systems with post-flight analyses to mass spectrometer and gas chromatograph systems employing various methods for measuring and identifying the sulfur gases during flight. Sampling schedules for the techniques ranged from integrated collections over periods as long as 50 minutes to 1- to 3-minute samples every 10 or 15 minutes. Several of the techniques provided measurements of more than one sulfur gas. As was the case for earlier CITE-1 and -2 tests, instruments employing different detection principles were involved in each of the sulfur intercomparisons. Intercomparison of measurements obtained by instruments employing different detection principles is one approach to add credibility to the measurement of low levels of trace gases as well as to provide confidence in both new and existing technology. The majority of the intercomparison results were for mixing ratios below 200 parts-per-trillion (pptv) and, thus, are important to validating current measurement capabilities at low concentrations normally encountered in clean and remote areas of the troposphere. Sulfur dioxide intercomparisons included mixing ratios to the ppbv levels. Carbonyl sulfide results were at the 300 to 600 pptv level; i.e., nominal ambient values. Also included in the intercomparison measurement scenario were a host of supporting measurements (i.e., ozone, nitrogen oxides, carbon monoxide, total sulfur, aerosols, etc.) for purposes of (1) interpreting the intercomparison results (i.e., correlation of any noted instrument disagreement with the chemical composition of the measurement environment) and (2) providing supporting chemical data to meet CITE-3 science objectives of studying ozone/sulfur photochemistry, diurnal cycles, etc.



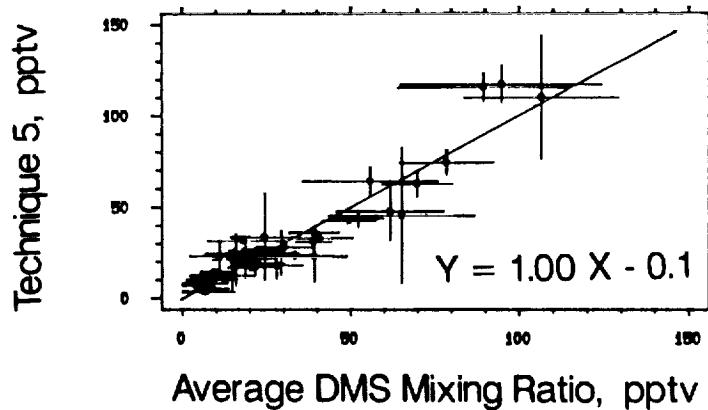
Results show good agreement among techniques for DMS, H₂S, and CS₂, from near the detection limit of the instruments (few ppt) to 100 to 200 pptv (upper limits of the intercomparisons). For example, DMS instrument agreement was on the average about 10 pptv among the instruments and was within stated accuracy and precision of the techniques (typically about 20%). Figure 1 shows the DMS results where data from different techniques are plotted versus the average DMS. The average is the arithmetic mean of the values reported from all the techniques. Plotted with the data point are the 1-sigma values for the average. Linear regression results are also given for each panel of the figure. Carbonyl sulfide results also showed good agreement for the 300- to 600-pptv range of concentrations investigated. Results suggest that each technique, regardless of its sampling period, provides equally valid measurements of the respective species. Apparently, such is not the case for SO₂. The initial analyses of the SO₂ intercomparison data suggested that ambient variability of SO₂ combined with the different temporal sampling schedules of the techniques were influencing the results and that, in many cases, differences between SO₂ values reported by the various techniques may be the result of SO₂ ambient variability. Additional analyses are being performed to separate ambient variability/temporal overlap influences from instrument intercomparison results. While these analyses are not yet complete, results suggest that there are some significant biases among one or more of the techniques which cannot be attributed to ambient variations and sample temporal overlap. On the other hand, results also suggest that for equally valid measurement techniques (i.e., no bias between techniques), the different sampling schedules combined with ambient variations can result in significantly different reported values of SO₂.



a) Technique 2

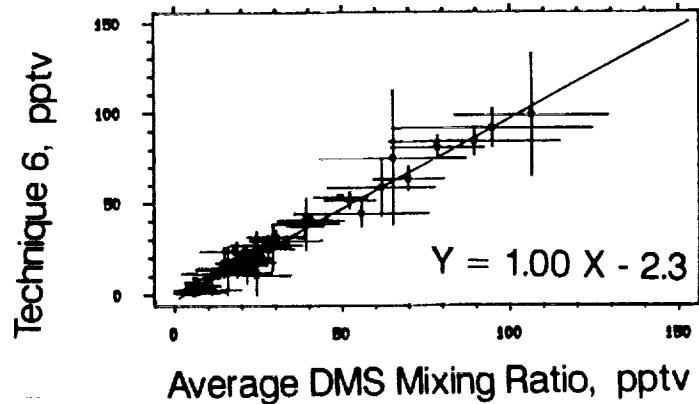


b) Technique 3

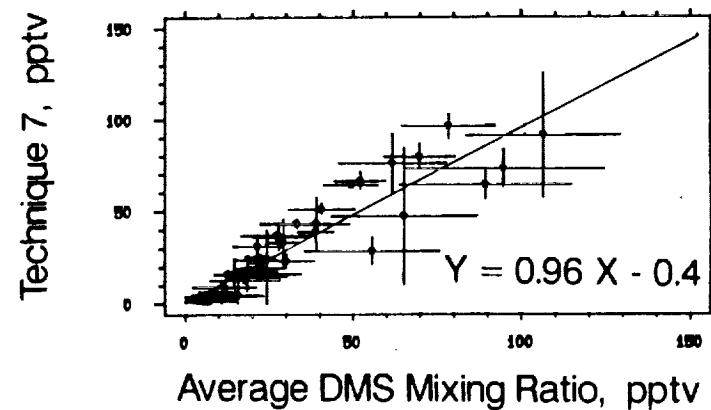


c) Technique 5

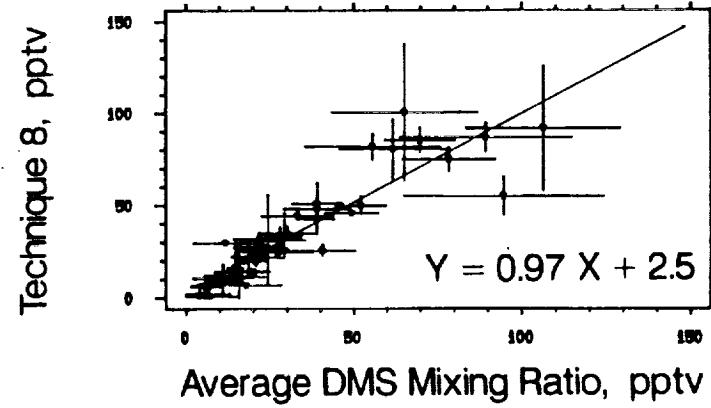
Figure 1. - Results of DMS Intercomparisons



d) Technique 6



e) Technique 7



f) Technique 8

Figure 1. - Concluded.